Synthesis of ZnO Nanoparticles and Investigation of the Ionic Template Effect on Their Size and Shape

Kamellia Nejati a,*, Zolfaghar Rezvani b, Rafat Pakizevand a

a Department of Chemistry, Payam Noor University, Tabriz, I.R. Iran
b Department of Chemistry, Faculty of Science, Azarbaijan University of Tabriz Moallem, Tabriz, I.R. Iran

(Received 12 October 2010, Accepted 18 January 2011)

Nanorods of ZnO have been selectively produced in a simple aqueous system prepared by mixing Zn(NO3)2 and NaOH solutions. Also, semi-spherical ZnO nanoparticles have been obtained by adding KNO3 and K2SO4 solutions to the Zn(NO3)2/NaOH mother solutions at different molar ratios of KNO3/Zn(NO3)2 and K2SO4/Zn(NO3)2, but with using LiNO3 at different molar ratios, the nanoparticles shape was different and not semi-spherical. The products have been characterized by X-ray diffraction (XRD) and FT-IR spectroscopy. The XRD patterns of samples were in agreement with that of the typical wurtzite structure ZnO and the sharp diffraction peaks indicated good crystallinity of the ZnO nanoparticles. The morphologies of the particles have been studied with a scanning electron microscope (SEM) and a transmission electron microscope (TEM), and their average size has been determined by means of an X-ray line-broadening method using the Scherrer equation. The results showed that the presence of K2SO4, KNO3 or LiNO3 led to the formation of slightly smaller ZnO nanoparticles. Chemical component analysis by energy-dispersive spectroscopy (EDS) showed that the ZnO nanoparticles were free from impurities.

Keywords: Nanorod, Semi-spherical, ZnO, Ionic Template, Particle Size

Introduction

Nanostructured ZnO materials have received broad attention due to their distinguished performances [1] in electronics [2], optics [2,3], and photonics [4]. ZnO is a key technological material. The lack of a center of symmetry in wurtzite, combined with strong electromechanical coupling, results in pronounced piezoelectric and pyroelectric properties and the consequent use of ZnO in mechanical actuators and piezoelectric sensors. The high exciton binding energy (60 meV) in ZnO crystals ensures efficient excitonic emission at room temperature [5]. The properties of ZnO particles are very important, and in the literature numerous reports can be found related to preparation methods and potential or practical applications, for example, as catalysts in ceramics, cosmetics, and in the paint and rubber industries [6].

The size and morphology of ZnO are important parameters in determining the physical and physicochemical properties of ZnO crystals [7]. Various kinds of nanoscale morphologies, such as spherical particles [8], rods [9], whiskers [10], and other characteristic shapes have been fabricated.

The preparation of zinc oxide nanoparticles from solution by the precipitation method involves the reaction of zinc salts, such as Zn(NO3)2, Zn(CH3COO)2·2H2O, ZnSO4, etc., with basic solutions containing LiOH, NH4OH, NaOH, etc. [6, 11]. In general, the synthesis of ZnO nanoparticles

*Corresponding author:
E-mail: nejati_k@yahoo.com
Tel: +98 411 382 0979, Fax: +98 411 543 1472

www.SID.ir
from aqueous solutions starts with a reaction between Zn$^{2+}$ and hydroxide ions, which is followed by an aggregation process.

In this paper, we present a simple method for regulating the shapes and average sizes of ZnO nanoparticles by adding KNO$_3$, K$_2$SO$_4$ or LiNO$_3$ solutions to Zn(NO$_3$)$_2$/NaOH solution at different KNO$_3$/Zn(NO$_3$)$_2$, K$_2$SO$_4$/Zn(NO$_3$)$_2$ and LiNO$_3$/Zn(NO$_3$)$_2$ molar ratios.

**Experimental**

**Materials and apparatus**

All salts (Zn(NO$_3$)$_2$, K$_2$SO$_4$, KNO$_3$, LiNO$_3$ and NaOH) were purchased from Merck chemical company.

All characterizations were carried out at room temperature. ZnO crystal structures were characterized by X-ray diffractometry (XRD; Bruker AXS model D8 Advance) using CuK$_\alpha$ radiation in the Bragg angle range 30–70° at 40 kV and 35 mA and rate of 0.04 degree in 4 seconds. The broadening was calculated from the (101) diffraction peak and the particles size were estimated from the Scherrer equation [12]. The morphology of the ZnO particles were observed by means of scanning electron microscope (SEM; LEO 440 i EDS). FT-IR spectra were recorded on a Shimadzu 8400s spectrophotometer from samples in KBr pellets.

**Preparation of ZnO nanoparticles**

ZnO nanoparticles were prepared in a similar manner as described elsewhere [7]. Thus, a 0.2 M solution of zinc nitrate and a 4.0 M alkali solution of sodium hydroxide were prepared by dissolving zinc nitrate tetrahydrate Zn(NO$_3$)$_2$·4H$_2$O and NaOH, respectively, in deionized water. To prepare ZnO nanoparticles, 25.0 mL of the alkali solution (4.0 M NaOH) was dropped at an approximate rate of 5 mL/min into a mother solution prepared by mixing 25 mL of 0.2 M Zn(NO$_3$)$_2$ solution and 50.0 mL of deionized water with stirring. The final pH of the mixture was fixed at 13 because highly basic conditions are conducive to the direct preparation of ZnO crystals (Equations 1-3).

\[
\begin{align*}
Zn(NO_3)_2 & \rightarrow Zn^{2+} + 2NO_3^- \quad (1) \\
Zn^{2+} + 2OH^- & \rightarrow Zn(OH)_2 \quad (2) \\
Zn(OH)_2 & \rightarrow ZnO + H_2O \quad (3)
\end{align*}
\]

On maintaining the mixture at 60°C, precipitation occurred 2 h after mixing the solutions. The products obtained by centrifugation were washed with deionized water and then dried at 60°C in air.

On the other hand, to investigate the ionic template effect on the size and shape of the particles, we prepared ZnO by mixing 25 mL of 0.2 M Zn(NO$_3$)$_2$ solution, mL of 4.0 M NaOH solution, and 25 mL of an additional solution of either potassium nitrate (KNO$_3$), potassium sulfate (K$_2$SO$_4$) or lithium nitrate (LiNO$_3$) at molar ratios (KNO$_3$:Zn(NO$_3$)$_2$, K$_2$SO$_4$:Zn(NO$_3$)$_2$ or LiNO$_3$:Zn(NO$_3$)$_2$) of 0.5, 1.0, 2.0, and 5.0. Just like, on keeping the mixture at 60 °C, precipitation occurred 2 h after mixing the solutions. The products were collected by centrifugation, washed with deionized water, and then dried at 60 °C in air.

**Results and discussion**

**XRD**

X-ray powder diffraction patterns of ZnO nanoparticles are illustrated in Fig. 1. Pattern 1a was obtained from the ZnO nanoparticles prepared according to the method described elsewhere [7]. Patterns 1b–m were obtained from ZnO nanoparticles prepared in the presence of additional solutions of KNO$_3$, K$_2$SO$_4$ and LiNO$_3$ at different molar ratios. The XRD patterns of all of these samples are in agreement with that of the typical wurtzite structure ZnO (hexagonal phase, space group P6$_3$mc, and JCPDS no. 36-1451) [1].

The sharp diffraction peaks apparent in the figures indicate good crystallinity of the ZnO nanoparticles. No characteristic peaks of any other phase of ZnO or of any impurity were observed. This result indicates the high purity of the ZnO nanoparticles, which was further confirmed by EDS analysis (Fig. 2). The obtained ZnO particles were found to exhibit similar characteristic XRD peaks, even though they adopted different morphologies.
The average size of the particles was determined by means of the X-ray line-broadening method using the Scherrer equation. The results are shown in Table 1. The results show that the presence of K$_2$SO$_4$, KNO$_3$ or LiNO$_3$ leads to the formation of slightly smaller ZnO nanoparticles. With increasing of KNO$_3$, K$_2$SO$_4$ and LiNO$_3$ concentrations, the mean size of particles is reduced slightly.

**FT-IR**

The IR spectra of samples of ZnO particles are generally influenced by the particle size and morphology [13]. Fig. 3 shows the FT-IR spectra of the synthesized ZnO particles. The peaks at $\nu = 670$ and 555 cm$^{-1}$ are related to the stretching vibrations of Zn–O bonds [13]. The peak at 3405 cm$^{-1}$ indicates the presence of –OH residue, probably due to atmospheric moisture [14].

**SEM**

The morphologies of ZnO nanoparticles obtained with any ionic template as well as in the presence of KNO$_3$, K$_2$SO$_4$ and LiNO$_3$ solutions at different molar ratios were studied by TEM and SEM (Fig. 4). In the absence of potassium nitrate, potassium sulfate or lithium nitrate, nanorods were obtained as shown in Fig. 4a.

---

**Fig. 1.** X-ray diffraction patterns of (a) ZnO obtained according to the method described in ref. [7], and ZnO obtained in the presence of KNO$_3$ with molar ratios KNO$_3$/Zn(NO$_3$)$_2$ of (b) 1:2, (c) 1:1, (d) 2:1, and (e) 5:1, and in the presence of K$_2$SO$_4$ with molar ratios K$_2$SO$_4$/Zn(NO$_3$)$_2$ of (f) 1:2, (g) 1:1, (h) 2:1, and (i) 5:1, and in the presence of LiNO$_3$ with molar ratios LiNO$_3$/Zn(NO$_3$)$_2$ of (j) 1:2, (k) 1:1, (l) 2:1, and (m) 5:1.
Table 1. The average crystallite size of ZnO nanoparticles produced under different reaction conditions.

<table>
<thead>
<tr>
<th>Obtained in the presence of:</th>
<th>Average size of nanoparticles (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>any ionic template</td>
<td>99</td>
</tr>
<tr>
<td>KNO₃ with a KNO₃/Zn(NO₃)₂ molar ratio of 1:2</td>
<td>96</td>
</tr>
<tr>
<td>KNO₃ with a KNO₃/Zn(NO₃)₂ molar ratio of 1:1</td>
<td>95</td>
</tr>
<tr>
<td>KNO₃ with a KNO₃/Zn(NO₃)₂ molar ratio of 2:1</td>
<td>89</td>
</tr>
<tr>
<td>KNO₃ with a KNO₃/Zn(NO₃)₂ molar ratio of 5:1</td>
<td>82</td>
</tr>
<tr>
<td>K₂SO₄ with a K₂SO₄/Zn(NO₃)₂ molar ratio of 1:2</td>
<td>94</td>
</tr>
<tr>
<td>K₂SO₄ with a K₂SO₄/Zn(NO₃)₂ molar ratio of 1:1</td>
<td>91</td>
</tr>
<tr>
<td>K₂SO₄ with a K₂SO₄/Zn(NO₃)₂ molar ratio of 2:1</td>
<td>89</td>
</tr>
<tr>
<td>K₂SO₄ with a K₂SO₄/Zn(NO₃)₂ molar ratio of 5:1</td>
<td>80</td>
</tr>
<tr>
<td>LiNO₃ with a LiNO₃/ Zn(NO₃)₂ molar ratio of 1:2</td>
<td>130</td>
</tr>
<tr>
<td>LiNO₃ with a LiNO₃/ Zn(NO₃)₂ molar ratio of 1:1</td>
<td>123</td>
</tr>
<tr>
<td>LiNO₃ with a LiNO₃/ Zn(NO₃)₂ molar ratio of 2:1</td>
<td>120</td>
</tr>
<tr>
<td>LiNO₃ with a LiNO₃/ Zn(NO₃)₂ molar ratio of 5:1</td>
<td>115</td>
</tr>
</tbody>
</table>
When KNO$_3$ was added to the solution at different KNO$_3$/Zn(NO$_3$)$_2$ molar ratios, the shape of the ZnO crystals changed from rods to semi-spherical, as exemplified in Fig. 4b. It is clear from the above results that the ZnO crystal undergoes structure evolution on increasing the KNO$_3$ in the solution and in all concentrations of KNO$_3$ the resultant particles were nanometric grains with a semi-spherical shape. To ascertain whether this morphology change is caused by potassium or nitrate, further experiments were carried out with K$_2$SO$_4$ and LiNO$_3$ at different molar ratios. The representative SEM image in Fig. 4c (related to addition of K$_2$SO$_4$) shows that the morphology of the resultant nanoparticles resembled that of the particles obtained in the presence of KNO$_3$ (Fig. 4b). Increasing of KNO$_3$ or K$_2$SO$_4$ concentration has no clear effect on particles shape and in all concentrations, morphology of particles is semi-spherical. But the morphology of ZnO nanoparticles obtained in the presence of LiNO$_3$ in all concentrations is quite different from the one with KNO$_3$ or K$_2$SO$_4$ and not semi-spherical (Fig. 4d). Based on our observations from these experiments, we can conclude that K$^+$ is the key factor in controlling the morphologies of ZnO crystals and NO$_3^-$ or SO$_4^{2-}$ anions do not control crystals morphologies.

EDS analysis of the nanocrystals obtained showed that no potassium or lithium was present in the precipitates obtained at different molar ratios.

Fig. 4. TEM image of ZnO nanoparticles obtained in the presence of any ionic template (a). SEM images of ZnO nanoparticles obtained in the presence of (b) KNO$_3$ with a 1:1 molar ratio of KNO$_3$/Zn(NO$_3$)$_2$, (c) K$_2$SO$_4$ with a 2:1 molar ratio of K$_2$SO$_4$/Zn(NO$_3$)$_2$ and (d) LiNO$_3$ with a 1:2 molar ratio of LiNO$_3$/Zn(NO$_3$)$_2$. 
Therefore, these ions must have been present in the residual solution. Also, it is well known that wurtzite ZnO crystals mainly adopt a hexagonal configuration (space group $P6_{3}mc$). The structure of ZnO can be simply described as a number of alternating planes composed of tetrahedral coordinated O$^{2-}$ and Zn$^{2+}$ ions, stacked alternatively along the c-axis. Another important characteristic of ZnO is the polar surfaces. The most common polar surface is the basal plane. The oppositely charged ions produce positively charged Zn-(0001) and negatively charged O-(0001$^{-}$) polar surfaces. Beside the most typical $\{0001\}$ polar surfaces that are terminated with Zn and oxygen, respectively $\{011^{-1}\}$ and $\{110^{-1}\}$ and $\{011^{-1}\}$ are also polar surfaces [5, 16-17]. Fig. 5 describes planes of ZnO crystals from the side view (Fig. 5a) and the top view (Fig. 5b) [15].

![Diagram of ZnO crystals](image)

**Fig. 5.** Schematic diagram of ZnO crystals (a) side view of planes, (b) top view of planes.

In the absence of K$^+$, Zn$^{2+}$ is absorbed on the $\{0001\}$ planes and reacts with OH$^{-}$ to form ZnO. Therefore, the ZnO crystals show growth orientated along the $\{0001\}$ direction. With the addition of KNO$_3$ or K$_2$SO$_4$ to the solution, however, K$^+$ competes with Zn$^{2+}$ for adsorption sites on the $\{0001\}$ plane and thereby reduces the growth rate in this direction. Thus, we observed semi-spherical crystals, as shown in Fig. 4b,c. Competition of K$^+$ with Zn$^{2+}$ inhibited adsorption of Zn$^{2+}$ on the $\{0001\}$ plane, and forced more Zn$^{2+}$ to be adsorbed onto the six side planes. This may be the reason for the slower ZnO growth along $\{0001\}$ and faster growth along the side planes, which shortens the ZnO crystal length and increases its diameter.

In all reactions, the time for growth was kept fixed at 2 h. The ZnO particles were found to reach their steady-state sizes after 2 h in our experiments. Also, the NaOH concentration was kept fixed for all experiments and the temperature was 60 $^\circ$C throughout.

**Conclusion**

We have presented a simple, easy to perform, and reproducible method for synthesizing zinc oxide (ZnO) nanoparticles. We have been able to change the size and shape of ZnO nanocrystals by adding of KNO$_3$, K$_2$SO$_4$ and LiNO$_3$ solutions to the Zn(NO$_3$)$_2$/NaOH mother solution. The mean size of the particles slightly reduced with increasing the concentration of KNO$_3$, K$_2$SO$_4$ or LiNO$_3$ in solution. The morphology of the ZnO particles without any ionic template was rod-like and in presence of all concentrations of KNO$_3$ or K$_2$SO$_4$ varied to semispherical shape. In the case of LiNO$_3$, the shape of the particles was quiet different from the one with KNO$_3$ or K$_2$SO$_4$ and not semi-spherical.
Syntheses of ZnO Nanoparticles and Investigation of the Ionic Template Effect

References